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THE INTERACTION OF ALKOXY SILANE COUPLING AGENTS
WITH SILICA SURFACES

BY

R. L. KAAS AND J. L. KARDOS

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THE INTERACTION OF ALKOXY SILANE COUPLING AGENTS
WITH SILICA SURFACES

BY
R. L. KAAS AND J. L. KARDOS

AUGUST 1970

MONSANTO/WASHINGTON UNIVERSITY ASSOCIATION
HIGH PERFORMANCE COMPOSITES PROGRAM
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ROLF BUCHDAHL, PROGRAM MANAGER

MONSANTO RESEARCH CORPORATION
800 NORTH LINDBERGH BOULEVARD
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FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. Rolf Buchdahl. (Phone: Area Code 314-694-4721).

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THE INTERACTION OF ALKOXY SILANE COUPLING AGENTS WITH SILICA SURFACES

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Abstract

The interactions of γ -aminopropyltriethoxy silane (A-1100), γ -methacryloxytrimethoxy silane (A-174), γ -glycidoxytrimethoxy silane (A-187), and ethyltriethoxy silane (A-15) with silica surfaces have been studied by means of infrared spectroscopy. The results indicate that the major force holding the silane to the silica surface after application from dilute solutions is primary chemical bonding. These bonds are formed by a condensation reaction between silanols on the hydrolyzed form of the silane and hydroxyl groups on the silica surface. In the case of the amino-silane (A-1100), hydrogen bonding was found to exist but was of minor importance in bonding the silane to the surface. In studying the effects of the addition of water, acetic acid, or n-propylamine to the treating solution, it was found that n-propylamine has a unique catalytic effect on this reaction. This catalytic effect explains the observation that γ -aminopropyltriethoxy silane is more reactive than the other silanes studied. It is felt that silanes not containing an amine group can be made more effective if they are applied in the presence of an amine catalyst.

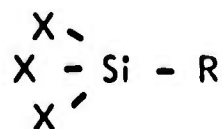
THE INTERACTION OF ALKOXY-SILANE COUPLING AGENTS WITH SILICA SURFACES

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Introduction

Early in the development of fiberglass-reinforced plastics it was found that the mechanical properties of these materials were significantly affected by humidity. It was obvious that if these materials were to be used in a humid atmosphere it would be necessary to modify the reinforcement in some way in order to increase the adhesion of the resin to the reinforcement. This, in part, led to the use of coupling agents. A coupling agent, in general, is any substance which can interact either chemically or physically with both the glass surface and the resin matrix to increase the degree of adhesion. Ideally, one would like to modify the glass surface so that the resin can attach itself to the surface with some degree of chemical bonding. With this goal in mind, many coupling agents have been produced which have two different kinds of functionality on the same molecule; one type is chosen to preferentially react with the glass surface and another type is chosen to react with the active groups of the resin.

The most effective and most widely used coupling agents are the organosilanes having the general structure,



where the X groups are either alkoxy or halogen groups, usually methoxy, ethoxy, or chloro. These groups hydrolyze in the presence of water to form silanols which in turn can condense with the silanols present on the glass surface to form siloxane linkages ($\text{Si} - \text{O} - \text{Si}$). The group R is chosen to be resinophilic. It may be vinyl, γ -methacryloxy-propyl, γ -amino-propyl, γ -glycidoxy-propyl, or a variety of other organo-functional groups. A number of different silanes are commercially available so that the R-group functionality can be matched with the functionality of the resin of interest. For example, when using polyester resins, coupling agents containing unsaturated groups such as vinyl or methacryloxy are usually used so that the unsaturated groups of the coupling agent can copolymerize with the unsaturated groups present in the polyester resin. Likewise, the amino-propyl and glycidoxy silanes are usually used with the epoxy resins since silanes with these groups can react with the active groups in the epoxy. Evidence supporting the hypothesis of chemical bonding to the glass has been obtained by several workers [1-4].

In a recent state-of-the-art paper, Plueddemann [5] has interpreted a wide variety of experimental results from silane coupling agent studies in terms of a mechanism which he describes as a dynamic equilibrium between forming and breaking bonds to the filler surface, with water playing an important role in the process.

Interactions other than chemical reaction can occur between the coupling agent and the surface. Complex silane molecules containing polar groups may become hydrogen bonded to the surface. A condensation reaction may also occur between silane molecules rather than between a silane molecule and the surface so that a siloxane polymer is formed. This siloxane polymer may subsequently become bonded to the surface by reaction with surface hydroxyls.

Since glass is the most widely used reinforcement, the major emphasis to date has been placed on studying adhesion to glass surfaces. Organosilane surface treatments have been found to improve the resin-to-glass bond, especially under conditions of high temperature and humidity. However, the mechanisms responsible for the improved adhesion are rather poorly understood. The importance of the presence of adsorbed water on the glass surface and of effects such as hydrogen bonding and polymer formation is not known. A number of different proposals have been made in addition to chemical bonding to account for the action of silane coupling agents. These other theories include: (a) a restricted layer theory [6-9] which assumes that the surface of the reinforcement somehow affects the mobility of the polymer in a region near the interfaces. This restriction of the polymer mobility alters the mechanical properties of the resin matrix and hence the properties of the composite; (b) a preferential adsorption theory [10] which suggests that certain components of the resin are selectively attracted to the surfaces of the reinforcement. This would result in a gradient in the chemical composition of the resin near the interface and again result in altered mechanical properties; (c) a coefficient of friction theory [11] which asserts that bonding at the glass-resin interface is not important but that frictional resistance to relative movement between the resin and the reinforcement controls the mechanical properties of the composite. This theory considers the role of the coupling agent to be that of altering the coefficient of friction between the resin and the reinforcements; and finally (d) a theory based on wetting and surface energy effects [12-14] which assumes that the coupling agents produce more intimate contact between the resin and the reinforcement by improving the wetting of the reinforcement.

Much of the past work has approached the problem of studying the interfacial properties of reinforced plastics through studies of mechanical properties. This approach

can demonstrate the effectiveness of the various surface treatments and application procedures, but it is not sensitive or selective enough to independently provide an accurate description of the interactions occurring at the interfaces.

In order to better understand the effects of coupling agents and possibly to suggest new surface treatments, it is necessary to understand the mechanisms of the interactions of silane molecules with the glass surface as well as the parameters which affect these mechanisms. With this in mind, a model system, using very pure, high surface area silica as an analog of the glass surfaces, has been studied by the technique of infrared spectroscopy. The infrared spectroscopy approach was chosen because it is potentially a powerful technique which can supply information about molecular structure and orientation not provided by other methods. In most cases, the nature of the spectrum will allow a clear distinction to be made between chemisorption and physical adsorption. Thus, the changes which occur in the spectra from sample to sample can be used to determine the type of interactions involved.

Infrared spectroscopy has been previously used to study the adsorption of silanes and other materials on silica surfaces [15-18]. These studies have concentrated primarily on the vapor phase chemisorption of simple organo-silanes on silica surfaces [15, 16] and on the adsorption of common organic materials on degassed silica surfaces [17, 18]. The excellent study by White [15] examined the reactions of the surface hydroxyl groups of silica with a series of chlorosilanes, including phenyltrichlorosilane, trimethyl chlorosilane, ethyltrichlorosilane, and vinyltrichlorosilane. The bulk of this work was concerned with vapor phase chemisorption of the chlorosilanes. Some results for adsorption from solution were shown; however, only the relatively simple silane molecules listed above were considered.

Our research efforts have been to expand the scope of White's work by attempting to describe and explain the behavior of more complex silane molecules as they are adsorbed on silica surfaces from solution. Unlike the simple molecules considered by White, the more complex silanes considered here can exhibit several kinds of interactions with the surface. These include: (a) chemical reaction which yields primary bonds to the silica surfaces, (b) hydrogen bonding between polar end groups and the surface hydroxyl groups, and (c) reaction between silane molecules forming siloxane polymers. The silanes which have been studied are γ -aminopropyltriethoxy silane [Union Carbide A-1100; $(\text{CH}_3\text{CH}_2\text{-O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$], γ -methacryloxypropyltrimethoxy silane [Union Carbide A-174; $(\text{CH}_3\text{-O})_3\text{-Si-(CH}_2)_3\text{-O-C(=O)-CH=CH}_2$], γ -glycidoxypropyltrimethoxy silane [Union Carbide A-187; $(\text{CH}_3\text{O})_3\text{-Si-(CH}_2)_3\text{-O-CH}_2\text{-CH(CH}_2\text{O)-CH}_2$], and ethyltriethoxysilane [Union Carbide A-15; $(\text{CH}_3\text{-O})_3\text{SiCH}_2\text{-CH}_3$]. These are all alkoxysilanes which behave differently than the chlorosilanes considered by White.

Experimental

The interactions of the silanes with Cabosil*, a very pure, high surface area silica (99.8 percent SiO_2 , BET surface area-- $150 \text{ m}^2/\text{g}$), were studied using infrared spectroscopy. Silica wafers, approximately 0.15 mm thick, were prepared by pressing 65 mg of Cabosil between discs of aluminum foil in a one-inch diameter die at room temperature and a pressure of approximately 12,000 psi. The aluminum foil was stripped from the fragile silica wafers before treatment with solutions of the various materials of interest.

*Godfrey L. Cabot, Incorporated, Boston, Massachusetts.

Unless otherwise specified, the treatments were applied to the surfaces of the silica wafers from 1 percent by weight solutions in analytical reagent grade acetone. From one to six wafers were treated for various times in a petri dish containing 50 ml of the desired solution. Upon removal from the treating solution, the wafers were briefly rinsed with clean acetone to remove any entrained material and then allowed to dry. All these treatments were carried out at room temperature. After the surface treatment was applied, some of the samples were immediately analyzed with standard infrared techniques while others were evacuated for five hours in a specially designed cell which provided vacuums of approximately 3×10^{-5} torr at temperatures up to about 500°C. The cell flanges were fitted with NaCl windows so that the infrared spectrum could be recorded without exposing the sample to humid laboratory air. After evacuation at elevated temperatures, the cell was allowed to cool while the vacuum was maintained. The spectra were then recorded at room temperature while the sample remained under vacuum in the cell.

The spectra were recorded in the region from 4000 to 1300 cm^{-1} on a Perkin-Elmer Model 457 grating infrared spectrometer. A scan rate of 400 $\text{cm}^{-1}/\text{min}$ was used. Reference beam attenuation was used when recording the spectra of samples in the vacuum cell. This was necessary to compensate for the attenuation of the sample beam as it passed through the cell.

Results and Discussion

Figure 1 shows the effect of the evacuation temperature on the spectrum of untreated cabosil wafers. The 25°C spectrum shows bands characteristic of the surface

hydroxyls on silica. The very sharp band at 3745 cm^{-1} is due to those hydroxyl groups which are not associated with adsorbed water or with adjacent hydroxyl groups. These hydroxyl groups are called free hydroxyls. The broad band at $3,500\text{ cm}^{-1}$ is due to those surface hydroxyls which are hydrogen bonded with one another or are associated with adsorbed water. As the temperature of evacuation is increased, the adsorbed water is driven from the surface. This is evidenced by the shifting and narrowing of the associated hydroxyl band and a slight intensification of the free hydroxyl band as the temperature is increased.

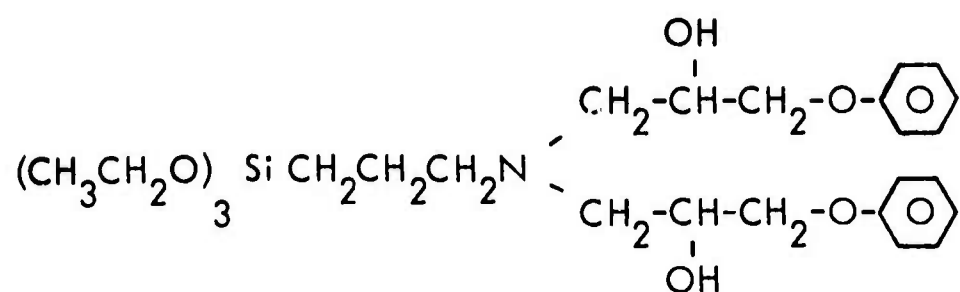
The complete spectrum of the silica wafer also shows two other bands. A band at 1850 cm^{-1} is attributed to the siloxane linkages in the bulk of the silica [19] and is unaffected by the surface treatments; therefore, it can be used as an internal thickness band. Likewise, a band in the region 1600 to 1650 cm^{-1} is believed to be due to the structure of the bulk silica [19].

When A-1100 is applied to the silica wafers from a 1 percent acetone solution for 24 hours, the spectra shown in Figure 2 are obtained. The spectrum of the sample evacuated at 25°C shows a disappearance of the free hydroxyl band at 3745 cm^{-1} and the formation of a very broad band due to hydrogen bonding between the amine group of the A-1100 molecule and the surface hydroxyls. The bands at 2940 and 2880 cm^{-1} are due to C-H stretching absorptions and indicate the presence of A-1100 on the surface. When the sample is evacuated at 460°C , hydrogen bonding decreases and the free hydroxyl band reappears at a reduced intensity. Evacuation at this temperature has apparently caused a slight reduction in the intensity of the C-H absorption. The retention of the hydrocarbon and the reduced intensity of the free hydroxyl band suggest that

the A-1100 molecule has been tied to the surface by reaction with the free hydroxyls. However, at this point we cannot rule out the possibility that the original loss of free hydroxyls was due to hydrogen bonding between the amine group of A-1100 and the surface. Also, intermolecular reaction forming the siloxane polymer could have occurred, but this would not have affected the free hydroxyls on the silica surface.

When silica wafers are treated with A-1100 for various times, the depletion of the free hydroxyls on the silica surface can be followed by monitoring the intensity of the band at 3745 cm^{-1} . Variations in sample thickness can be accounted for by dividing the free hydroxyl absorbance by the absorbance of the internal thickness band at 1850 cm^{-1} . Figure 3 shows this normalized free hydroxyl absorbance for samples whose spectra were recorded at room temperature without evacuation. As the treatment time is increased through the range shown, the free hydroxyl absorbance decreases linearly on the semi-log plot indicating first-order kinetics. Also, as the free hydroxyls are depleted, increased hydrocarbon absorption (not shown) and increased hydrogen bonding (indicated by broadening of the associated hydroxyl band) are observed. The fact that the free hydroxyl depletion follows first-order kinetics suggests that the hydrolyzed A-1100 molecules chemically react with the surface, but the possibility that the depletion is due to hydrogen bonding cannot be ignored.

In order to determine the importance of the hydrogen bonding of the amine end-groups of A-1100 with the surface, they were tied up through reaction with a monofunctional epoxy (1,2-epoxy-3-phenoxy propane) prior to treatment of the surface. The amine attacks the epoxy ring and a tertiary amine is formed with the structure shown below:



In this epoxidized form, A-1100 is much less likely to form hydrogen bonds with surface hydroxyls. The epoxidized A-1100 was prepared by adding a stoichiometric amount of the epoxy to a 10 percent solution of A-1100 in spectral-grade hexane. This mixture was then allowed to reflux in the hexane for 24 hours. The oily product formed a second phase which was separated and purified by extraction with fresh hexane,

When a sample treated with the epoxidized A-1100 is evacuated at room temperature, a dramatic decrease in hydrogen bonding compared to the normal A-1100 treatment is observed as shown in Figure 4; however, the free hydroxyls have also been depleted (compare with the 25°C spectrum in Figure 2). Figure 4 also shows bands at 2930 and 2880 cm^{-1} due to the presence of hydrocarbon. The presence of the phenyl group is indicated by the weak bands in the region 3100 to 3000 cm^{-1} and also by bands at about 1600 and 1500 cm^{-1} . After evacuation at 450°C the hydrogen bonding is further reduced, the hydrocarbon and phenyl absorption bands are only slightly reduced, and the free hydroxyl band appears at reduced intensity. By comparison with the spectra obtained for A-1100 on silica, these results indicate that a substantial amount of hydrogen bonding occurs between the A-1100 and the surface but that it is not the prime force holding the molecule to the surface. The depletion of free hydroxyls suggests that at least some of the silanols of the A-1100 have reacted with the surface and the molecules are then held to the surface by primary chemical bonds.

Next, in an attempt to demonstrate primary bonding more conclusively, the different functionalities of the A-1100 molecule were isolated on molecules containing only one kind of functionality. The A-1100 molecule was, in essence, split in two parts by the use of analogs. N-propylamine was used as the model for the amine functionality of the A-1100 while ethyltriethoxysilane [Union Carbide A-15; $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_3$] was used to approximate the hydroxyl functionality. When n-propylamine was applied to the silica, the hydrogen bonding increased but the molecule was not strongly attached to the surface. This can be seen in Figure 5 which shows consecutive scans of the same sample under the same scanning conditions. Apparently 20 minutes of exposure to only the heat of the radiation beam in the spectrometer has driven much of the amine from the silica surfaces. Figure 6 shows the resulting spectra after a 24-hour treatment with A-15. One observes little reaction with the surface hydroxyls since the free hydroxyl band is still very strong and only small amounts of hydrocarbon are present, indicated by the weak bands at 2930 and 2880 cm^{-1} . Essentially the same results were obtained whether (a) the stoichiometric amount of water required to hydrolyze the ethoxy groups was added to the solution, (b) a large excess of water was present as in a 3:1 acetone-to-water mixed solvent, or (c) stoichiometric water along with 0.1 percent acetic acid was added to act as a catalyst for the hydrolysis reaction. The same results were obtained for treatment times as great as 100 hours. These results were unexpected on the basis of the prior conclusion that chemical bonding was the primary force holding the A-1100 molecule to the surface. In fact, they are completely contradictory and seem to undermine the entire basis of the chemical bonding theory.

However, when the silica wafers are treated for 90 hours with a 1 percent by weight solution of A-15 in acetone containing n-propylamine in a 1:1 mole ratio with the A-15,

infrared analysis yields the spectra of Figure 7 and the apparent contradiction is eliminated. It appears from these spectra that the silanol condensation reaction has occurred since the free hydroxyl band has disappeared and strong hydrocarbon absorption bands are present. When the sample is heated to 450°C under vacuum, the hydrocarbon absorption remains strong while the associated hydroxyl band is greatly reduced. The amine present in this solution has apparently acted as an effective catalyst and caused reaction to occur between the silane and the surface hydroxyls. Subsequent evacuation at 450°C then removed the amine and adsorbed H₂O, resulting in a large decrease in hydrogen bonding and regeneration of a peak shoulder at 3745 cm⁻¹ due to newly formed free hydroxyls.

This amine catalysis of the reaction between A-15 and the silica surface appears to be a general phenomenon and can be extended to explain the behavior of A-1100 as well as other alkoxy silanes. Since A-1100 has the amine functionality on the molecule, it is reasonable to assert that A-1100 molecules self-catalyze their reaction with the surface. Thus, A-1100 forms primary chemical linkages to the silica surface more readily than other silanes. This can be seen from one viewpoint in Figure 8, which shows the effect of treatment time on the normalized free hydroxyl absorbance from the room temperature spectra of unevacuated samples. Neither the addition of n-propylamine nor the addition of water to the treating solution has a pronounced accelerating effect on the reaction between A-1100 and the surface.

On the other hand, the amine catalysis is strikingly obvious when silanes containing no amine are considered. Figures 9 and 10 show the normalized surface free hydroxyl absorbances for silica treated with γ -methacryloxy propyltrimethoxysilane (A-174) and γ -glycidoxy propyltrimethoxysilane (A-187), respectively. The spectra

used to generate these figures were obtained from samples which were not heated or evacuated. In these figures the effectiveness of the amine catalysis is compared with that of water and acetic acid. All catalyst materials were used at a 1:1 mole ratio with respect to silane. It can be seen from these figures that n-propylamine is decidedly more effective in accelerating the surface reaction than either water or acetic acid. In fact, neither water nor acetic acid appear to have any significant catalytic effect. From this, one can suggest that the acetic acid normally used as a catalyst in applying silane coupling agents be replaced with n-propylamine. Since the amine appears to increase the amount of reaction with the filler surface, it might be reasonable to expect that the coupling effectiveness of the silanes would be increased if they are applied from solutions containing an amine catalyst.

It has been observed [20] that the addition of n-propylamine when treating silica with ethyltriethoxysilane produces a more hydrophobic surface and a more stable H_2O contact angle. A solubility enhancing effect of amines on aqueous solutions of vinyltrimethoxysilanes has also been reported [21]. However, at this point the mechanism by which the amine catalyzes the reaction between alkoxy silanes and silica surfaces is not known. The amine could work by either aiding the hydrolysis of the alkoxy groups originally present on the silane or by accelerating the condensation between the hydrolyzed silane and the surface hydroxyls. The data presented here are not sufficient to determine which of these processes is the rate-determining step.

Conclusions

It is asserted that chemical bonding does occur between the A-1100 molecule and silica surfaces. This chemical bonding is the primary force holding the molecule to

the surface with hydrogen bonding playing only a minor role. Although definite evidence has not been presented here, it is felt that intermolecular condensation occurs between silane molecules to form a siloxane polymer film on the surface. This film is tied to the surface by chemical bonds formed by a condensation reaction between some of the silanols on the A-1100 molecules and the surface hydroxyls.

The amine catalysis of the reaction of an alkyl silane (A-15) with the surface suggests that there is a synergistic or self-catalysis effect when both the amine and the hydroxyl functionalities are combined on the same molecule. This is a fortunate effect since the rationale for using an amino-functional silane such as A-1100 was originally to match the functionality of the coupling agent with that of epoxy resins so that copolymerization can occur. The advantage of the self-catalysis of A-1100, to our knowledge, has not been recognized before.

Finally, the amine catalysis effect might be advantageously extended to the application of silanes such as A-174 and A-187 to glass surfaces. The amine could increase the number of chemical linkages to the glass surface and possibly yield composites of higher strength and better wet strength retention.

Acknowledgments

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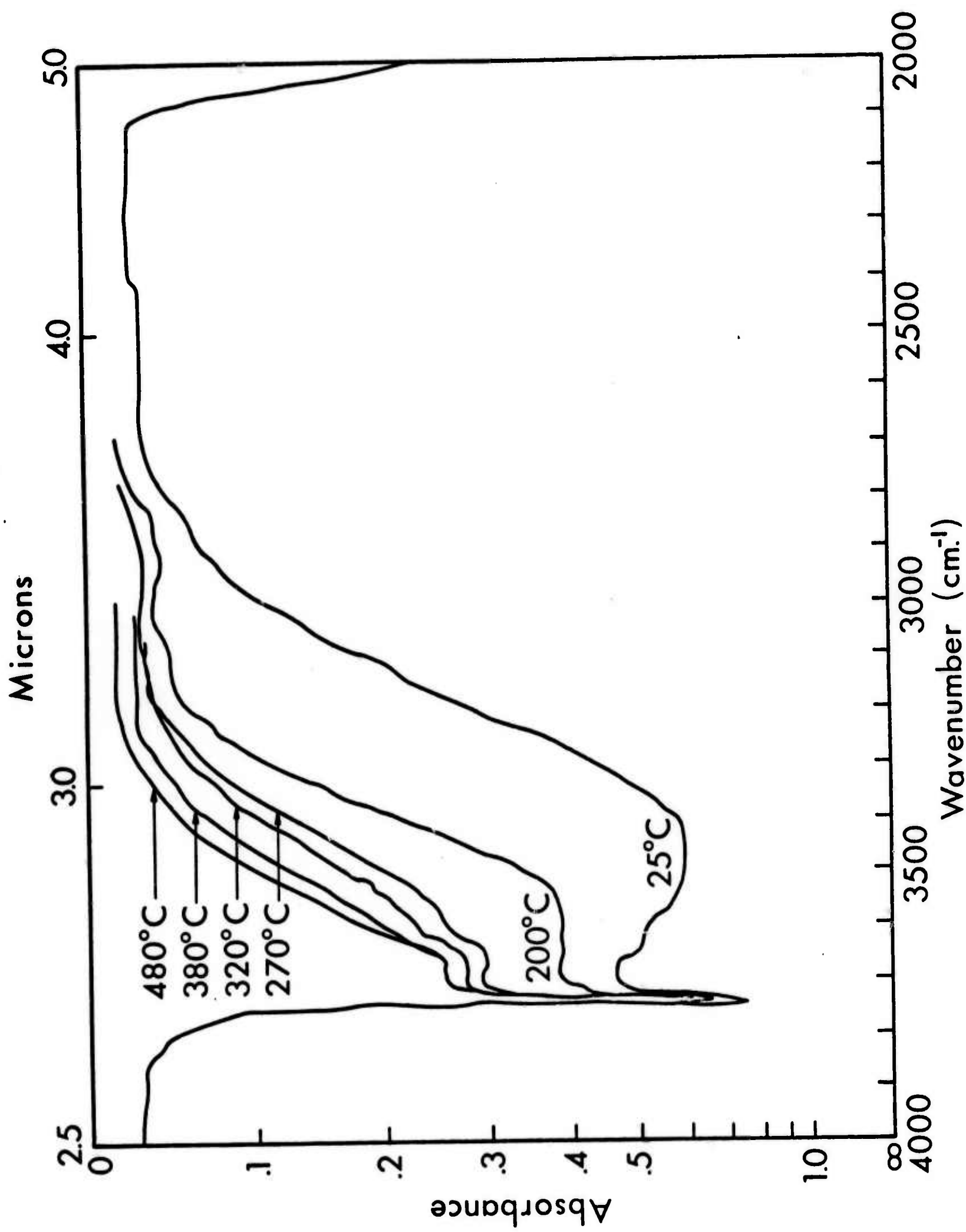


Figure 1 Effect of Evacuation Temperature on the Spectrum of Untreated Cabosil

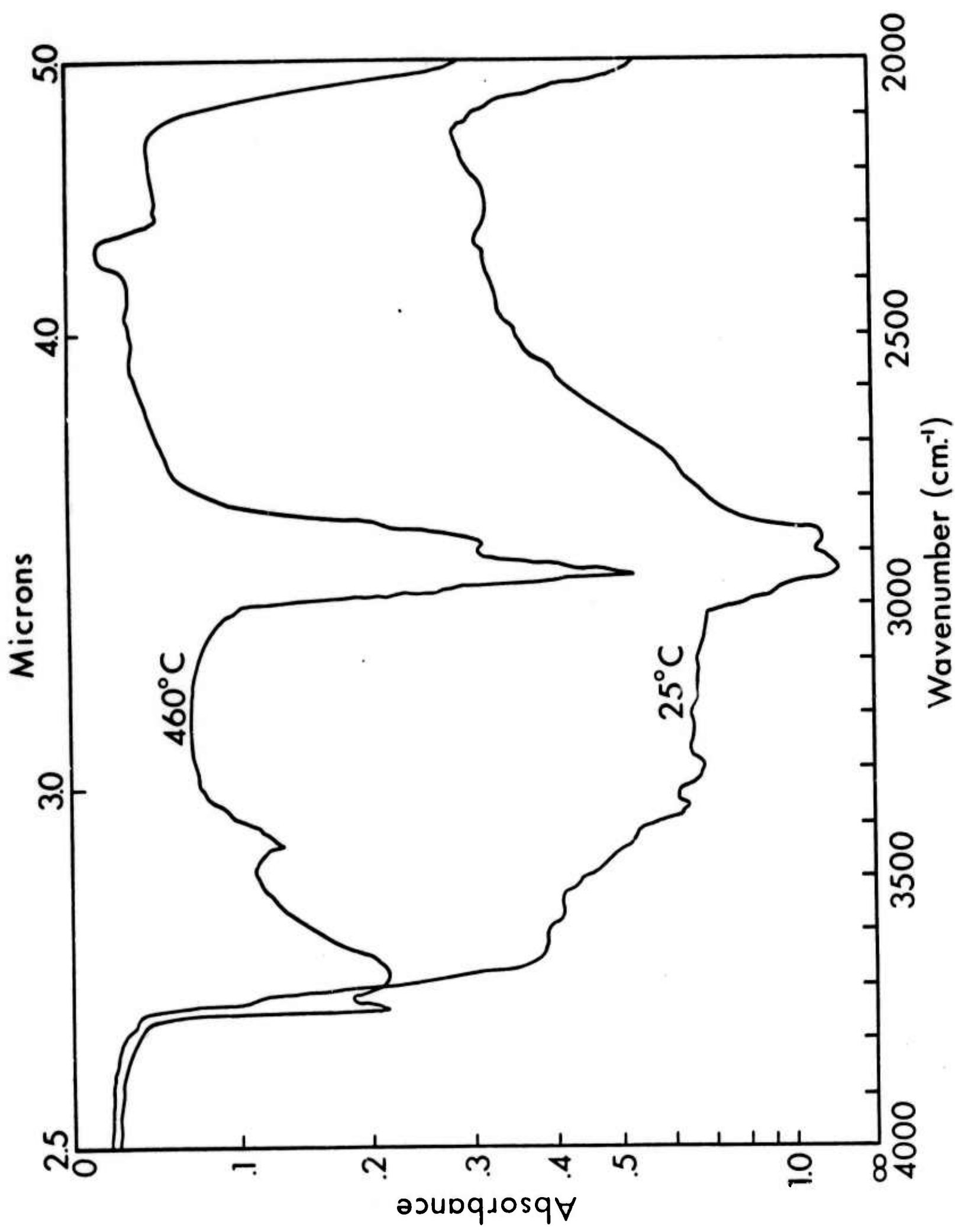


Figure 2 Spectra of Cabosil After Treatment With A-1100 for 24 Hours.

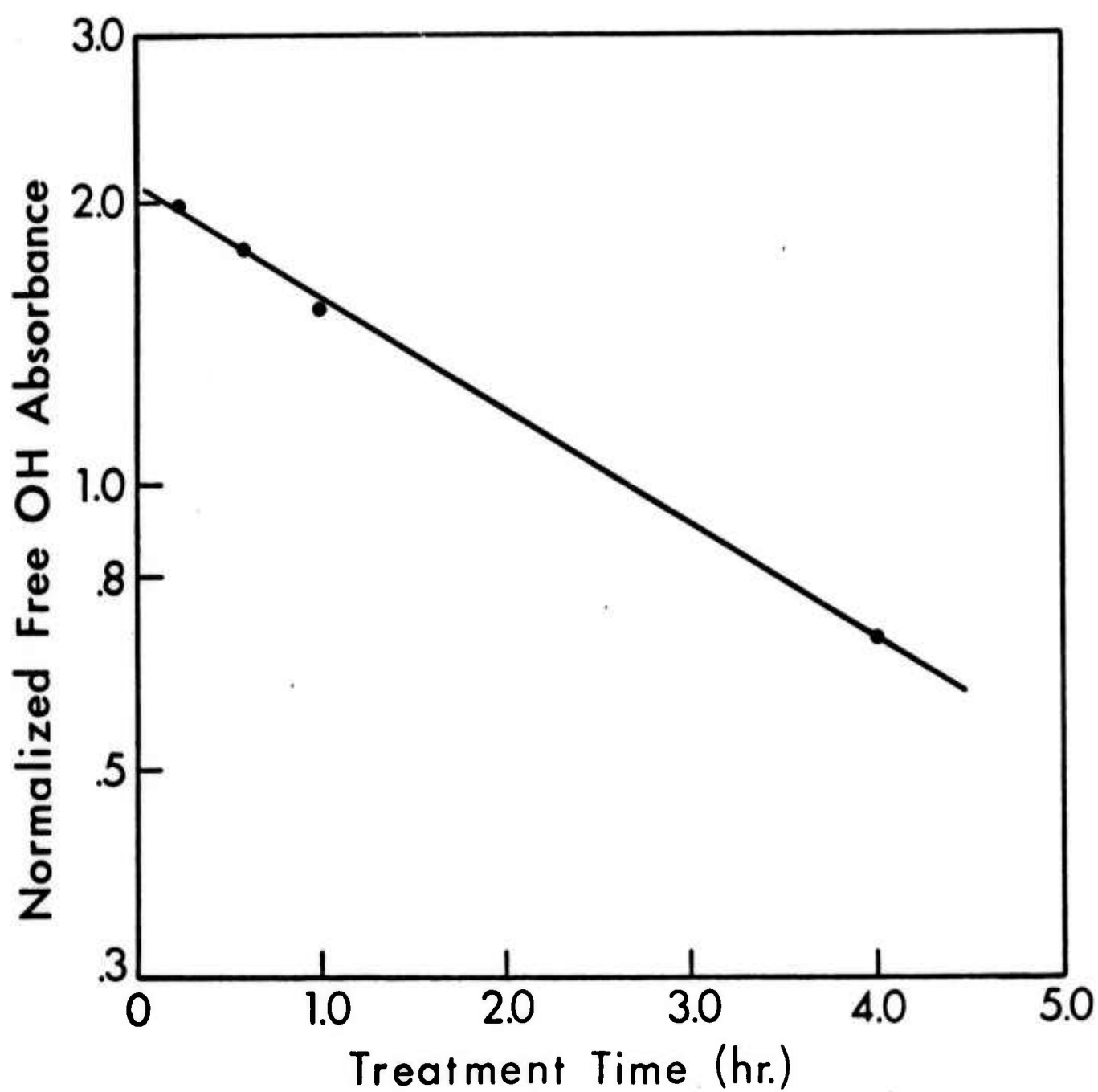


Figure 3 Effect of Treatment Time on the Reaction Between A-1100 and the Surface Hydroxyls.

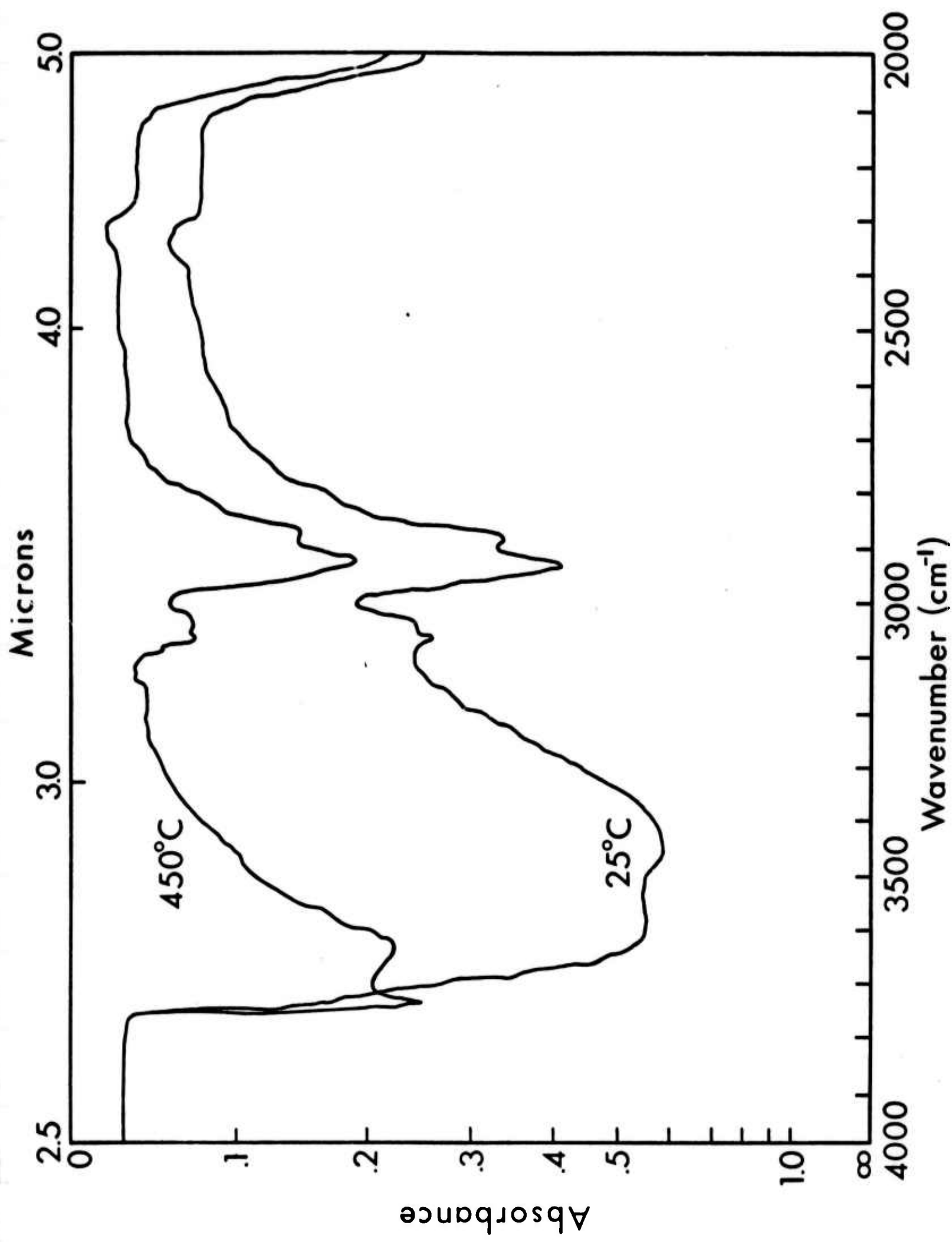


Figure 4 Spectra of Cabosil Treated With Epoxidized
A-1100 for 24 Hours.

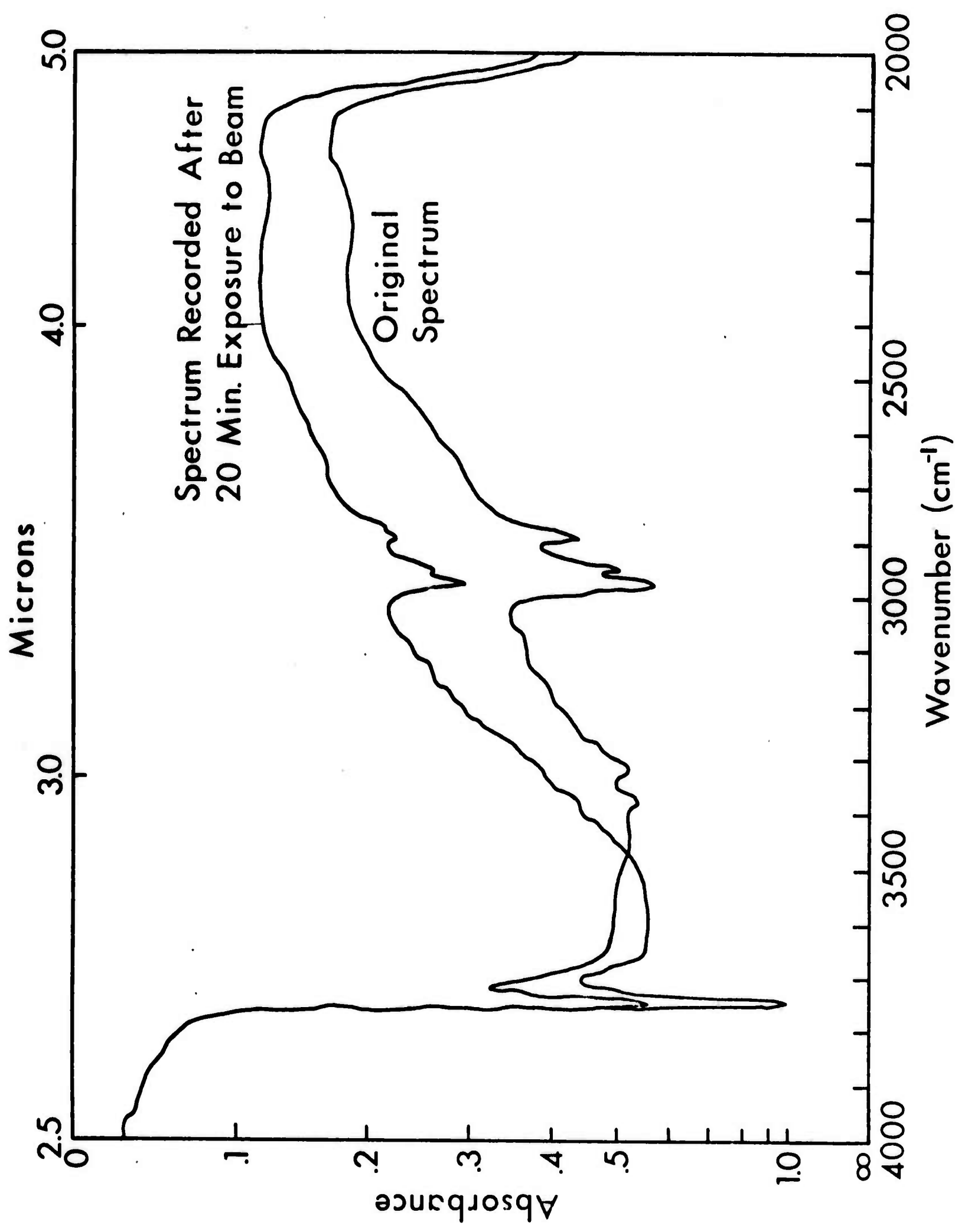


Figure 5 Spectra of Cabosil Treated With N-Propylamine

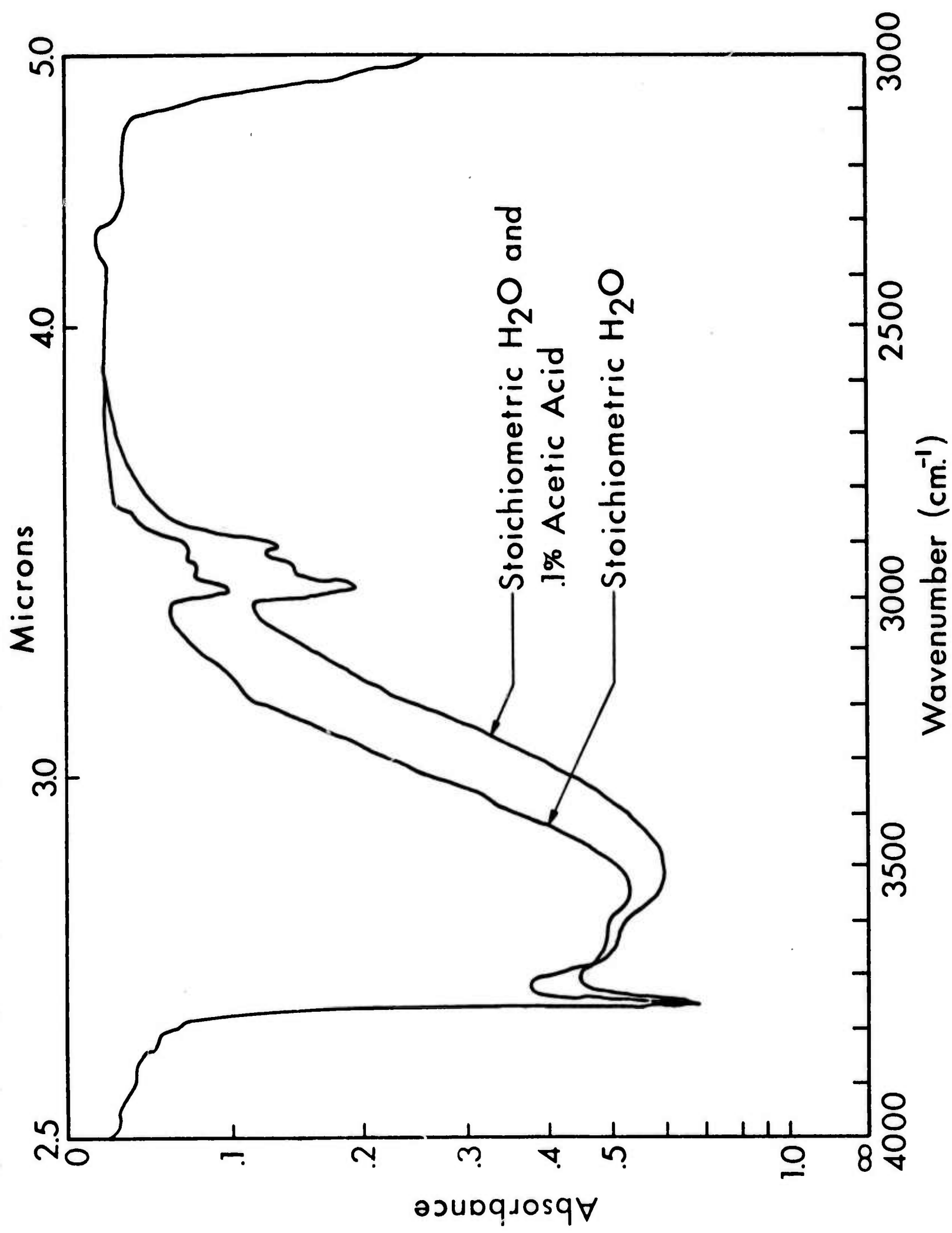


Figure 6 Spectra of Cabosil Treated With A-15

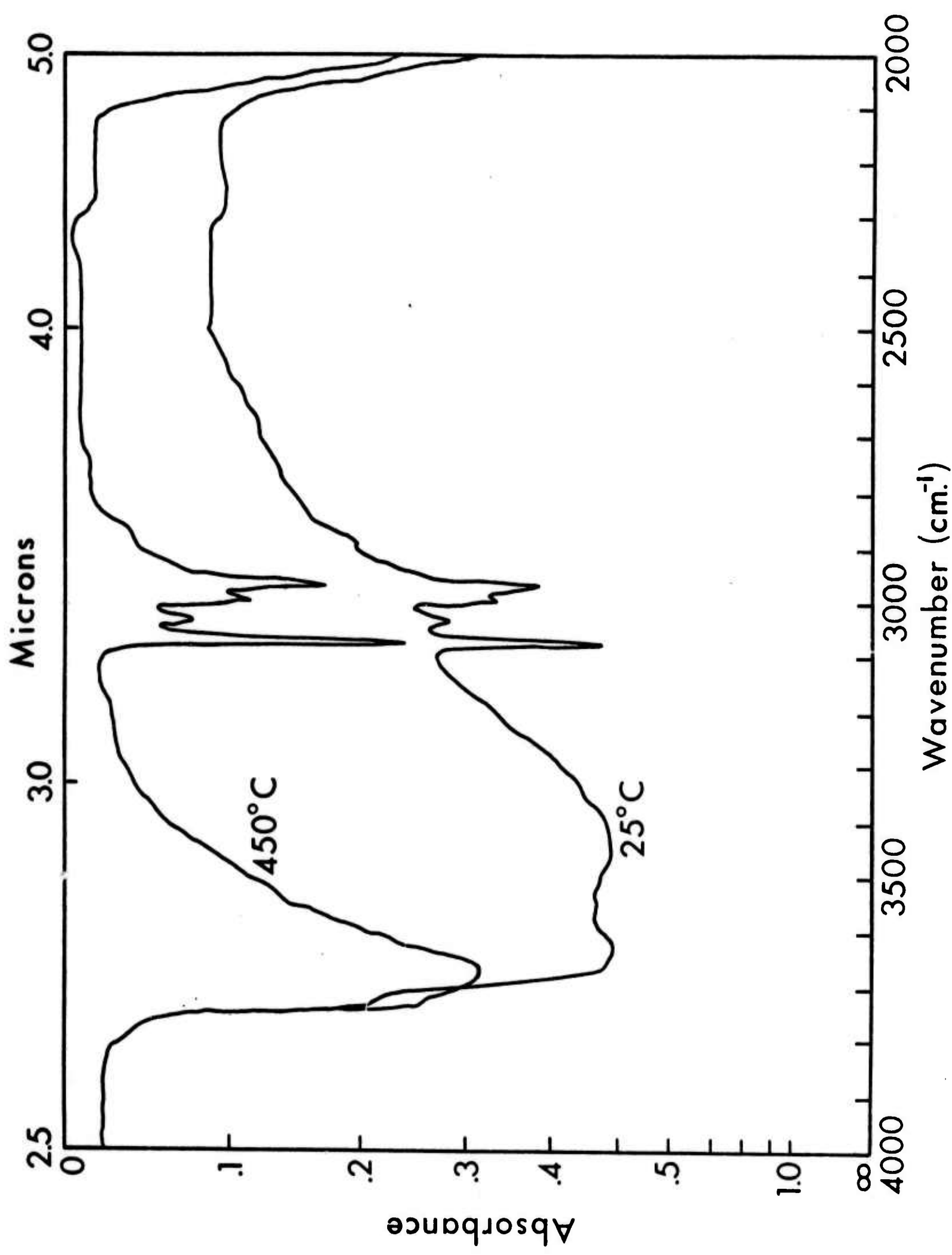


Figure 7 Spectra of Cabosil After a 90 Hour Treatment With
A-15 and n-Propylamine at 1:1 Mole Ratio.

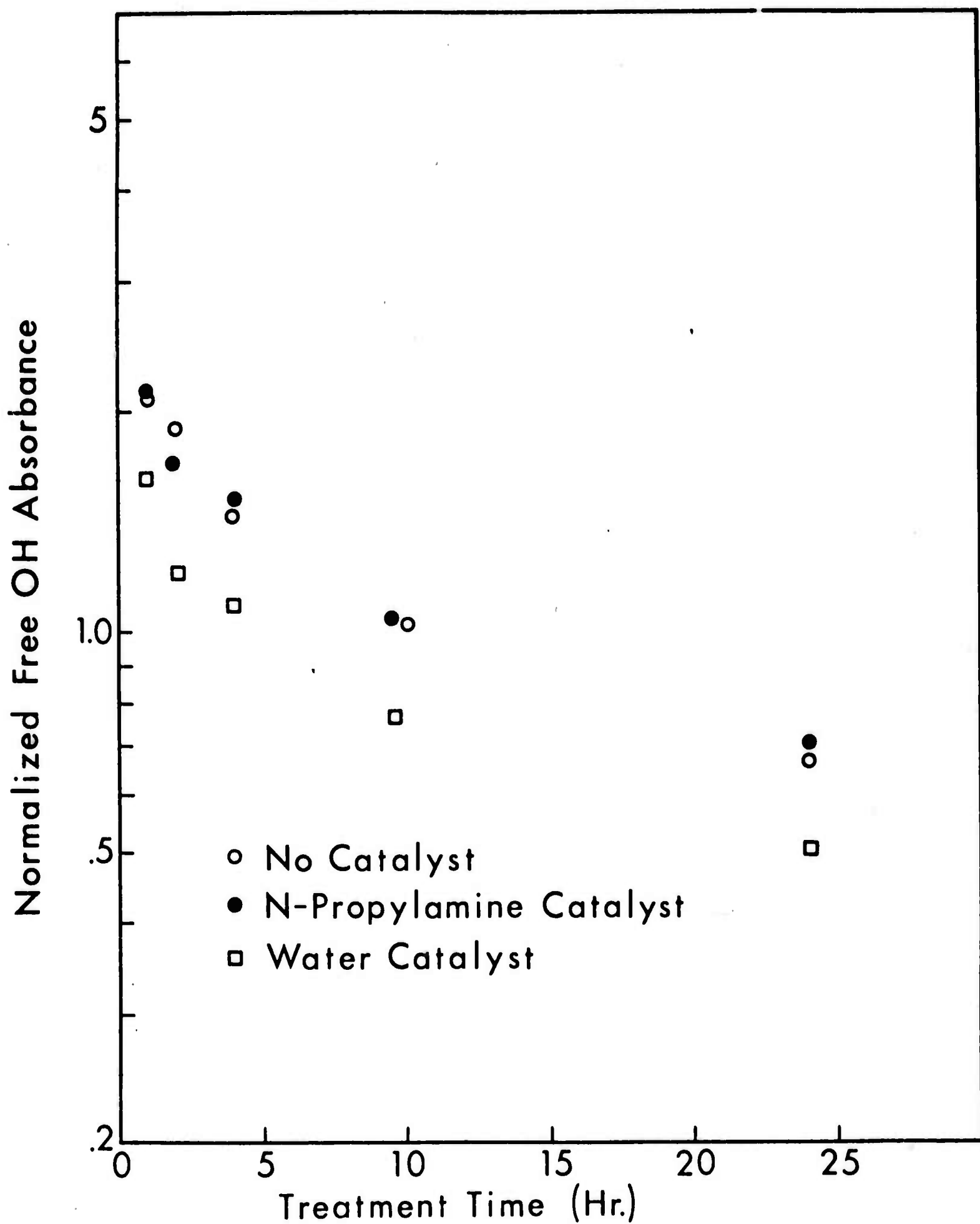


Figure 8 Effect of Catalyst on the Reaction Between A-1100 and the Silica Surface

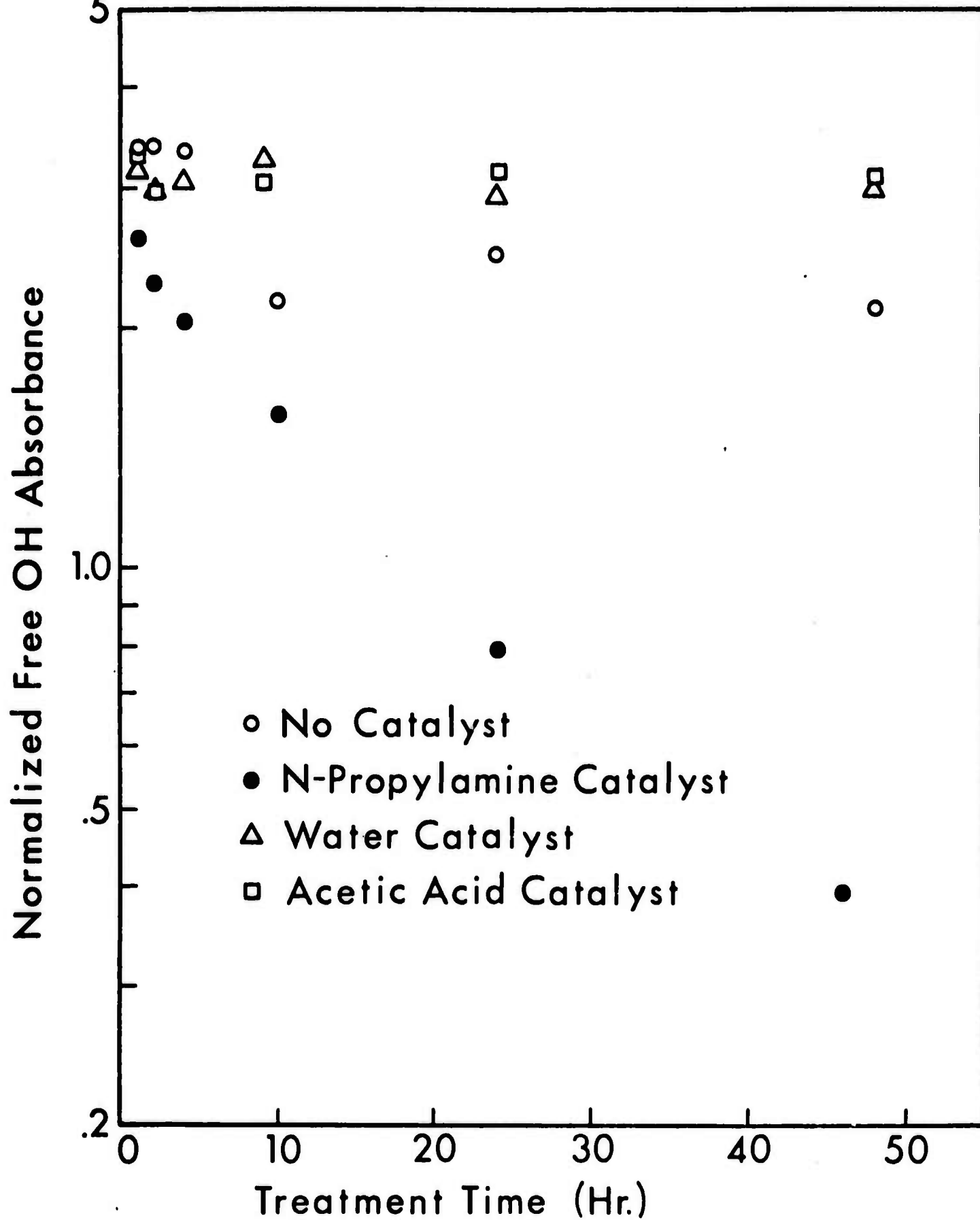


Figure 9 Effect of Catalyst on the Reaction Between A-174 and the Silica Surface

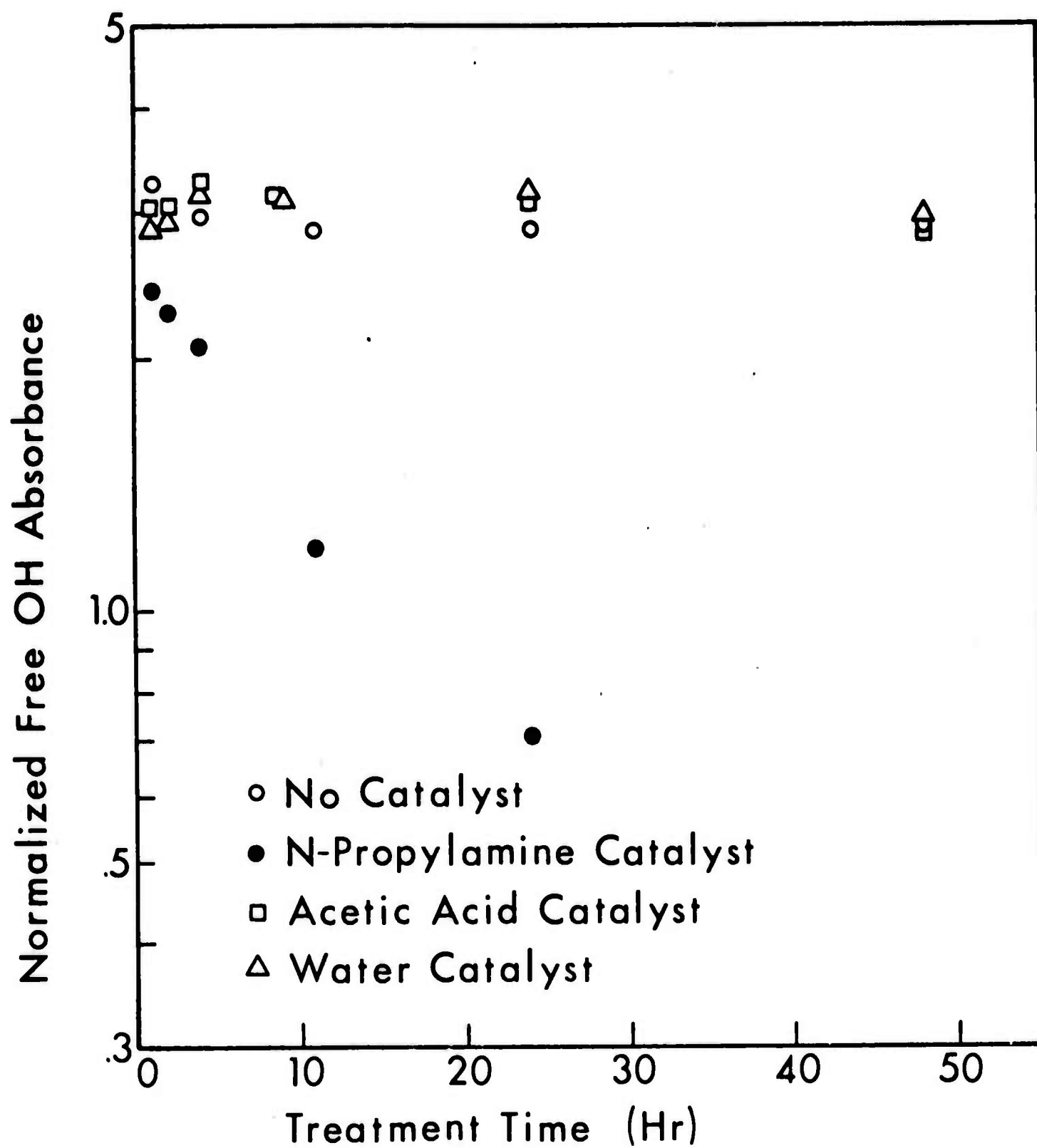


Figure 10 Effect of Catalyst on the Reaction Between A-187 and the Silica Surface

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13. ABSTRACT

The interactions of γ -aminopropyltriethoxy silane (A-1100), γ -methacryloxytrimethoxy silane (A-174), γ -glycidoxytrimethoxy silane (A-187), and ethyltriethoxy silane (A-15) with silica surfaces have been studied by means of infrared spectroscopy. The results indicate that the major force holding the silane to the silica surface after application from dilute solutions is primary chemical bonding. These bonds are formed by a condensation reaction between silanols on the hydrolyzed form of the silane and hydroxyl groups on the silica surface. In the case of the amino-silane (A-1100), hydrogen bonding was found to exist but was of minor importance in bonding the silane to the surface. In studying the effects of the addition of water, acetic acid, or n-propylamine to the treating solution, it was found that n-propylamine has a unique catalytic effect on this reaction. This catalytic effect explains the observation that γ -aminopropyltriethoxy silane is more reactive than the other silanes studied. It is felt that silanes not containing an amine group can be made more effective if they are applied in the presence of an amine catalyst.

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